

PATENT ABSTRACTS OF JAPAN

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(54) OXYGEN ABSORBENT/GENERATOR COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a composition which can rapidly liberate oxygen upon the application of voltage by including a cobalt complex and a conductive carbon. **SOLUTION:** This composition comprises a cobalt complex, desirably a cobalt (II) Schiff base complex or a mesotetrakis($\alpha,\alpha,\alpha,\alpha$ -o-pivalamidophenyl) porphyrinatocobalt (II) imidazole complex and a conductive carbon, the amount of the cobalt being desirably 55-85 wt.%. The cobalt (II) Schiff base complex is exemplified by N,N'-bis(salicylidene)ethylenediaminocobalt (II) or N,N'-bis(3-alkoxysalicylidene)ethylenediaminocobalt (II) and selectively combines with atmospheric O₂ to reversibly form an oxygen adduct of Co/O₂=2/1. The porphyrinatocobalt (II) imidazole complex forms an oxygen adduct of Co/O₂=1/1. Therefore, the desorption and re-absorption of oxygen are rapid.

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CLAIMS

[Claim(s)]

[Claim 1] The oxygen uptake and the generating body composition object characterized by consisting of a cobalt complex which generates oxygen by electrical-potential-difference impression, and conductive carbon.

[Claim 2] The oxygen uptake and the generating body composition object of claim 1 whose cobalt complex is a cobalt (II) Schiff base complex.

[Claim 3] The oxygen uptake and the generating body composition object of claim 1 whose cobalt complex is a meso tetrakis (alpha, alpha, alpha, alpha-omicron-PIBARU amide phenyl) porphyrinatocobalt (II) imidazole complex.

[Claim 4] Claim 1 of a constituent which is 55 - 85 % of the weight of cobalt complexes comparatively thru/or one oxygen uptake and generating body composition object of 3.

[Claim 5] Claim 1 whose configuration of the living body constituent from oxygen has the shape of the shape of a disk, and a sheet thru/or one oxygen uptake and generating body composition object of 4.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] Invention of this application relates to oxygen uptake and a generating body composition object. Invention of this application relates to the Plastic solid constituent of the small lightweight non-solvent which repeats oxygen gas with an electrical signal and can be generated in more detail.

[0002]

[Description of the Prior Art] oxygen -- combustion, an oxidation chemical reaction, and breathing -- an insufficient therapy, a cell culture, fish breeding, waste water treatment, etc. -- very -- width -- it is used widely. Generally, with 30 - 40%, although the others and purity which are supply by the oxygen cylinder, generating by disassembly of hydrogen peroxide solution, etc. are low, they are supplied using the separation generator by the adsorption process or the film method from air. however -- the approach of the former with high oxygen purity -- weight and ** -- it is high, and it is dealt with, and the raw material for a complicated bomb or oxygen evolution (for example, hydrogen peroxide solution) is required, and supply is limited. On the other hand, by the latter approach, although it is the separation supply which continued from air, the equipment and the operation power source of the medium size volume and weight are needed.

[0003]

[Problem(s) to be Solved by the Invention] Therefore, invention of this application solves the problem of the conventional technique as above, faces it offering the approach of repeating oxygen and carrying out separation supply from air, is very small and lightweight, and makes it a technical problem to offer the constituent which can generate pure oxygen promptly by the electrical-potential-difference impression by the commercial dry cell.

[0004]

[Means for Solving the Problem] Invention of this application offers the oxygen uptake and the generating body composition object (claim 1) characterized by consisting of a cobalt complex which generates oxygen by electrical-potential-difference impression, and conductive carbon as what solves the above-mentioned technical problem. Moreover, the cobalt complex of invention of this application is a cobalt (II) Schiff base complex about the above-mentioned constituent (claim 2), A cobalt complex is a meso tetrakis (alpha, alpha, alpha, alpha-omicron-PIBARU amide phenyl) porphyrinatocobalt (II) imidazole complex (claim 3), It offers as the mode that the configuration of that it is [of said constituent] 55 - 85 % of the weight of cobalt complexes comparatively (claim 4) and said living body constituent from oxygen has the shape of the shape of a disk, and a sheet (claim 5) etc.

[0005] Invention of this above application is completed by the circumstances as follows. that is, artificers have first done research systematic about composition and the engine performance of the metal complex which can combine oxygen alternatively, quickly, and reversibly from air (as bibliography -- Tsuchida and Nishide -- "Topics in Current Chemistry" -- there are 132 s 64 - 99 pages (1986), the "Macromolecule-Metal Complexes" Springer publication (1995) written by editing besides Tsuchida, etc.). artificers considered as the liquid which can carry out separation conveyance of the oxygen from air as the use technique, and have materialized the film of an artificial red blood cell and the macromolecule complex which is made to penetrate oxygen and can be separated from

air etc. (as bibliography -- the John Wiley publication (1995) "written by [Artificial Red Cells]" Tsuchida, and Nishide and Tsuchida -- "Polymers for GasSeparation" -- there are Chapter 6, VCH publication (1992), etc.). On the other hand, similarly artificers have accumulated knowledge about the conductive ingredient (for example, there are Tsuchida, work "electronic function of macromolecule complex" Japan Scientific Societies Press (1990) edited by Nishide, etc. as bibliography). It found out that such scientific knowledge is synthesized, pure oxygen gas is promptly emitted when electrification of 1.5-several volts (V) is impressed to the cobalt complex which can combine oxygen alternatively and reversibly from air also in the state of solid phase, and the specific constituent which consists of conductive carbon, and a constituent repeated oxygen from air by electrical-potential-difference discharge, it repeated oxygen by absorption, and electrical-potential-difference impression and discharge again, and it could generate. Then, the experimental result that a mixed constituent with the conductive carbon which contains a cobalt (II) Schiff base complex as a result of examining wholeheartedly component and presentation of the living body from oxygen, and the gestalt of a constituent, or a meso tetrakis (alpha, alpha, alpha, alpha-omicron-PIBARU amide phenyl) porphyrinatocobalt (II) imidazole complex at 55 - 85% of the weight of a rate had the operation which was extremely excellent in the above-mentioned purpose was obtained. [0006] Invention of this application is completed based on such knowledge. The theoretic main point of invention of this application is summarized as follows.

- (1) Also in the state of solid phase, from air, the cobalt complex which constitutes the constituent of this invention joins together alternatively and reversibly, and can absorb oxygen.
- (2) The above-mentioned oxygen ligation reaction is exothermic reaction (enthalpy change accompanying a reaction a cobalt (II) Schiff base complex about -30 kcal/mol). With a cobalt (II) porphyrin complex, it is abbreviation-15 kcal/mol. That is, the static reaction of oxygen association inclines to an oxygen uptake side at low temperature, and inclines to an oxygen emission side at an elevated temperature.
- (3) The mixed constituent [carbon / conductive] of a specific presentation has a moderate electric resistance value, it carries out a temperature up by electrical-potential-difference impression by the very simple dry cell, it answers it, and pure oxygen generates it.
- (4) If the specific presentation mixture of a cobalt complex and conductive carbon is fabricated the shape of a disk, and in the shape of a sheet and electrical-potential-difference impression is carried out from both sides, a temperature up, i.e., oxygen evolution, is prompt.
- (5) By discharge of electrical-potential-difference impression, a constituent absorbs oxygen again from air corresponding to a temperature fall and it. That is, oxygen evolution and absorption can be repeatedly carried out by impression and discharge of an electrical potential difference.
- (6) Since oxygen uptake and generating occur as solid phase reaction, it can be constituted as equipment of a small light weight and a non-solvent.

[0007]

[Embodiment of the Invention] About invention of the oxygen uptake and the generating body composition object of this application that has the above description, the gestalt of that operation is explained in detail below. First, as that example of representation, the cobalt complex used in this invention is with 2 groups, and the 1st group is a cobalt (II) Schiff base complex. When an example is given, there is N and N'-bis(salicylidene) ethylene diamino cobalt (II), N, and N'-bis(3-alkoxy salicylidene) ethylene diamino cobalt (II), N, and N'-bis(salicylidene) tetramethyl ethylene diamino cobalt (II), N, and N'-bis(salicylidene) imino dipropylamino cobalt (II) etc. These cobalt (II) Schiff base complex combines oxygen alternatively from air, and generates the oxygen adduct of Co/O₂ =2/1 reversibly. Although the rate of oxygen association (absorption) is not large, composition of a Schiff base complex is easy, and the actuation life of oxygen uptake and desorption is long.

[0008] The 2nd group is a meso tetrakis (alpha, alpha, alpha, alpha-omicron-PIBARU amide phenyl) porphyrinatocobalt (II) imidazole complex. this porphyrinatocobalt (II) -- Collman ** -- it is the compounded compound (as reference -- J.P.Collman et al., and "Am.Chem.Soc. [J.]" 97-volume 1427 pages (1975)), and suitable imidazole derivatives and a suitable complex are constituted and oxygen capacity is discovered also in the state of solid phase. Although N-methyl imidazole, N-lauryl imidazole, N-benzyl imidazole, N-trityl imidazole, etc. are mentioned as imidazole derivatives, in order to prevent the evapotranspiration at the time of a temperature up, the boiling

point is a high derivative with low vapor pressure, and a derivative with small molecular weight is desirable to maintenance of the oxygen absorbed per unit. These porphyrinatocobalt (II) imidazole complexes generate the oxygen adduct of $\text{Co}/\text{O}_2 = 1/1$, and the desorption and resorption of oxygen are quick.

[0009] As long as the carbon powder mixed with a cobalt complex is conductivity, it may be based on which process. It grinds and uses, after washing and drying with the petroleum ether if needed. In the case of both, about 10-100 micrometers is suitable for the particle size of carbon powder and a cobalt complex from points of effectiveness, electric resistance, and oxygen gas, such as permeability. If a cobalt complex is a crystal, it will grind this, and will prepare and use it for the above-mentioned particle size. In the content of a cobalt complex, although 55 - 85% of the mixing ratio of a cobalt complex and carbon powder is suitable, it does not bar the outside of this range. Although the oxygen yield per constituent increases with a cobalt complex content, an electric resistance value is large and a temperature rise is no longer accepted. For example, N and an N'-bis (salicylidene) ethylene diamino cobalt (II) 70% constituent are 3ohms in electric resistance value, and the temperature up of them is promptly carried out to 80 degrees C by 6V impression, and they generate oxygen. The constituent of 60% of meso tetrakis (alpha, alpha, alpha, alpha-omicron-PIBARU amide phenyl) porphyrinatocobalt (II) benzyl imidazole complexes is 2ohms in resistance, and the temperature up of it is immediately carried out to 85 degrees C by 1.5V impression, and it generates oxygen.

[0010] Although a constituent may be fabricated in which configuration, in order to insert into a mesh electrode, to energize and to bring a temperature up to the whole constituent for a short time, the shape of the shape of a disk and a sheet is desirable. For example, a copper mesh is filled up on both sides of 0.8g of constituents at cylinder metal mold with a diameter of 2cm, and it is 120kg/cm² for 3 minutes. Pressurization obtains the disk (2mm in the diameter of 2cm, thickness) of a constituent. What is necessary is to connect lead wire from the center of a mesh of disk both sides, and just to carry out electrical-potential-difference impression by 1.5 dry cells (for the need to be accepted and for it to be a serial partly).

[0011] In addition, the constituent by this invention can present the application as an oxygen separating medium from air with an oxygen absorber etc. widely only as a living body from oxygen. An example is given below and this invention is explained still more concretely.

[0012]

[Example]

1 N of examples, N'-bis(salicylidene) ethylene diamino cobalt (II), and (the following, Co (salen) and a brief sketch) were compounded according to reference (M. Calvin "Am. Chem. Soc." 68-volume 2254 pages (1946)). [J.] It recrystallized [pyridine], it heated at 170 degrees C under reduced pressure on the 1st, and the pyridine was removed. Co (salen) The crystal was ground and particle size was arranged with 40-50 micrometers. Conductive carbon (the FUJIKURA KASEI carbo tightness, specific gravity 0.9-1.0) was dried under reduced pressure after hexane washing, and, similarly particle size was arranged with 40-50 micrometers. Co (salen) 0.57g and carbon 0.23g are fully mixed, and it inserts into a platinum mesh, and is 120kg/cm² for 3 minutes. Pressurization and Co (salen) It considered as the disk (2mm in the diameter of 2cm, thickness) of carbon. It is Co (salen) since every part of homogeneity and a disk fragment was coloring distribution of a cobalt element homogeneity within the disk at dark brown according to X-ray micro analysis. Good mixing and good Co (salen) of carbon Homogeneity distribution was checked. Co (salen) Although the mechanical strength of a disk was not large, there were not the below-mentioned temperature temperature up (room temperature -80 degree C) and damage in absorption / emission experiment of oxygen gas.

[0013] Lead wire was connected from the center of the platinum mesh of disk both sides, and the electric resistance value of a disk-like constituent was measured by the universal electric tester. Co (salen) Contents 100, 83, and 77 and the resistance in 71 or 67% of constituents in each were infinity and 2000, 34, 3, and 2ohm. Electrical-potential-difference 6V (four 1.5V dry-cells serial) were impressed, and the temperature inside a disk was measured with the thermistor. after 1 - 2 minutes -- constant temperature -- reaching -- Co (salen) Contents 100, 83, and 77 and 71 or 67% of interior temperature of each constituent were 25 (room temperature), 26, 55, and 83 or 50 degrees C. As

mentioned above, Co (salen) In high resistance, the constituent disk of 80% or more of contents is moderate conductivity, and unsuitableness and the disk of about 70% of contents were able to carry out the temperature up of it to 80 degrees C promptly by 6V impression.

[0014] Co (salen) The disk of 71% constituent of contents absorbed the oxygen of 22 ml/g (disk) under room temperature atmospheric air. This amount of absorption oxygen / Co (salen) A mole ratio is 0.49 and is absorption by the stoichiometry oxygen ligation reaction to a cobalt Schiff base complex. With applied voltage, the stationary temperature of this constituent disk rose in 1 - 2 minutes, and amounted to 80 degrees C in 6V impression (respectively [in impression / 3 / of V and 4.5V] 45 degrees C, 60 degrees C). The temperature up was answered and 18ml oxygen gas occurred from the disk (2mm in Co (salen) 71%, the diameter of 2cm, thickness) (per [this disk g] 22ml oxygen gas).

[0015] Generating of the above-mentioned oxygen gas was completed in 1 - 2 minutes. The disk was slowly lowered by discharge of electrical-potential-difference impression, and oxygen was again absorbed from air. This oxygen resorption took several hours. Generating of the oxygen gas by 6V impression and the oxygen resorption at the time of electrical-potential-difference discharge were repeatable 100 times or more. Moreover, oxygen evolution and absorption were not checked by 1 oxidation oxygen, a carbon dioxide, and 80% humidity, either.

As well as example 2 example 1, Co (salen) 5.7g and carbon 2.3g are mixed, a constituent is inserted into a 2x15cm copper mesh, and it is 100kg/cm². It considered as the Plastic solid of the shape of pressurization and a sheet (2x15cm, thickness of 2mm). After pulling out lead wire from copper mesh one end of sheet both sides, the sheet was considered as the roll of round-off and 2cm length of diameters of 2cm. When impressed 6V through lead wire, 170ml oxygen gas occurred in about 1 minute.

3 Ns of examples, N'-bis(3-ethoxy salicylidene) ethylene diamino cobalt (II), and (the following, Co (Esalen) and a brief sketch) were compounded according to reference (reference of the same Calvin and others as an example). It recrystallized and ground as well as the example 1, particle size was arranged, and similarly it inserted into carbon powder, mixing, and a platinum mesh, and fabricated on the disk with a diameter [of 2cm], and a thickness of 2mm.

[0016] the disk of the constituent of 62% of Co (Esalen) contents -- an example 1 -- the same -- 6V electrical-potential-difference impression -- about 1 minute -- up to 80 degrees C -- a temperature up -- carrying out -- per [Disk g] -- 18ml oxygen gas was generated. By discharge of electrical-potential-difference impression, resorption of the oxygen with a tales doses of 18ml was carried out from air in 25 minutes. This oxygen evolution and absorption were repeatable 100 times or more.

example 4 meso tetrakis (alpha, alpha, alpha, alpha-omicron-PIBARU amide phenyl) porphyrinatocobalt (II), and (the following, CoP and a brief sketch) -- said Collman ** -- it compounded according to reference. Under anoxia, 30ml of tetrahydrofuran solutions (CoP0.31g and N-benzyl imidazole 0.25g) was put, after adding adjustment and hexane 3ml 4 times every other hour. Since the crystal of a CoP benzyl imidazole complex (a following and CoP complex and brief sketch) deposited, it dried after washing by the hexane.

[0017] As well as the example 1, the CoP complex was arranged with about 50-micrometer particle size, and it mixed with this particle-size carbon powder. It inserts into a copper mesh and is 120kg/cm². It fabricated in the shape of a disk by pressurization. The CoP complex content 70 and the electric resistance value of 65 or 60% of class product disk are 1.6, 1.5, and 0.6ohm, and the temperature up of the 60% constituent of CoP complexes was carried out within 1 minute to 88 degrees C by electrical-potential-difference impression of 1.5V.

[0018] The disk of 60% constituent of CoP complexes generated 6.5ml [per disk g] oxygen gas by electrical-potential-difference impression of 1.5V (one dry cell). By electrical-potential-difference discharge, resorption of the oxygen with a tales doses of 6.5ml was carried out from air in about 3 minutes. This oxygen evolution and resorption were repeatable 50 times.

[0019]

[Effect of the Invention] The Plastic solid of the small lightweight non-solvent which can repeat oxygen gas with an electrical signal and can be generated by invention of this application is offered as explained in detail above.

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(54) OXYGEN ABSORBENT/GENERATOR COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a composition which can rapidly liberate oxygen upon the application of voltage by including a cobalt complex and a conductive carbon.
SOLUTION: This composition comprises a cobalt complex, desirably a cobalt (II) Schiff base complex or a mesotetrakis($\alpha,\alpha,\alpha,\alpha$ -o-pivalamidophenyl) porphyrinatocobalt (II) imidazole complex and a conductive carbon, the amount of the cobalt being desirably 55-85 wt%. The cobalt (II) Schiff base complex is exemplified by N,N'-bis(salicylidene)ethylenediaminocobalt (II) or N,N'-bis(3-alkoxysalicylidene)ethylenediaminocobalt (II) and selectively combines with atmospheric O₂ to reversibly form an oxygen adduct of Co/O₂=2/1. The porphyrinatocobalt (II) imidazole complex forms an oxygen adduct of Co/O₂=1/1. Therefore, the desorption and re-absorption of oxygen are rapid.

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(54)【発明の名称】 酸素吸収・発生体組成物

(57)【要約】

【課題】 酸素ガスを電気信号で繰り返し発生できる小形軽量無溶媒の成形体を提供する。

【解決手段】 電圧印加により酸素を発生する、コバルト錯体と導電性カーボンからなることを特徴とする酸素吸収・発生体組成物とする。

1

【特許請求の範囲】

【請求項1】 電圧印加により酸素を発生する、コバルト錯体と導電性カーボンからなることを特徴とする酸素吸收・発生体組成物。

【請求項2】 コバルト錯体が、コバルト(II)シップ塩基錯体である請求項1の酸素吸收・発生体組成物。

【請求項3】 コバルト錯体が、メソテトラキス(α, α, α, α-ο-ビバルアミドフェニル)ポルフィリナトコバルト(II)イミダゾール錯体である請求項1の酸素吸收・発生体組成物。

【請求項4】 組成物の割合が、コバルト錯体55～85重量%である請求項1ないし3のいずれかの酸素吸收・発生体組成物。

【請求項5】 酸素発生体組成物の形状が、ディスク状またはシート状である請求項1ないし4のいずれかの酸素吸收・発生体組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 この出願の発明は、酸素吸收・発生体組成物に関するものである。さらに詳しくは、この出願の発明は、酸素ガスを電気信号で繰り返し発生できる小形軽量無溶媒の成形体組成物に関する。

【0002】

【従来の技術】 酸素は燃焼、酸化化学反応、呼吸不全の療法、細胞培養や養魚、排水処理など極めて広く利用されている。一般には、酸素ボンベによる供給、過酸化水素水の分解による発生などのほか、純度は30～40%と低いものの空気から吸着法または膜法による分離発生装置を用いて供給されている。しかし、酸素純度の高い前者の方法では、重量、高高く、取り扱い煩雑なボンベ、または酸素発生のための原料(たとえば過酸化水素水)が必要であり、また供給は有限である。一方後者の方法では、空気からの連続した分離供給ではあるが、中型容積と重量の装置と稼働電源を必要とする。

【0003】

【発明が解決しようとする課題】 従ってこの出願の発明は、以上のとおりの従来技術の問題を解決し、空気から酸素を繰り返し分離供給する方法を供するに際し、極めて小型かつ軽量で、市販乾電池による電圧印加で速やかに純酸素を発生することのできる組成物を提供することを課題とするものである。

【0004】

【課題を解決するための手段】 この出願の発明は、上記の課題を解決するものとして、電圧印加により酸素を発生する、コバルト錯体と導電性カーボンからなることを特徴とする酸素吸收・発生体組成物(請求項1)を提供する。また、この出願の発明は、上記組成物について、コバルト錯体が、コバルト(II)シップ塩基錯体であること(請求項2)、コバルト錯体が、メソテトラキス(α, α, α, α-ο-ビバルアミドフェニル)ポルフ

2

ィリナトコバルト(II)イミダゾール錯体であること(請求項3)、前記組成物の割合が、コバルト錯体55～85重量%であること(請求項4)、前記酸素発生体組成物の形状が、ディスク状またはシート状であること(請求項5)等をその態様として提供する。

【0005】 以上のこの出願の発明は、次のとおりの経緯により完成されたものである。すなわち、まず、発明者らは、空気から酸素を選択的、迅速かつ可逆的に結合できる金属錯体の合成とその性能について系統的な研究

10 行ってきた(例えば、参考文献として土田・西出「Topics in Current Chemistry」132巻 64～99頁(1986)、土田他編著「Macromolecule-Metal Complexes」Springer出版(1995)等がある)。発明者らはその利用技術として、空気から酸素を分離運搬できる液体として人工赤血球、空気から酸素を透過せしめて分離できる高分子錯体の膜などを具体化してきた(例えば、参考文献として土田著「Artificial Red Cells」John Wiley出版(1995)、西出・土田「Polymers for Gas Separation」第6章、VCH出版(1992)等

20 がある)。他方、同じく発明者らは、導電性材料についても知見を蓄積してきた(例えば、参考文献として土田・西出編著「高分子錯体の電子機能」学会出版センター(1990)等がある)。このような学術知見を総合して、固相状態でも空気から選択的かつ可逆的に酸素を結合できるコバルト錯体と、導電性カーボンから成る特定の組成物に、1.5～数ボルト(V)の電化を印加したところ、速やかに純酸素ガスが放出され、かつ電圧解除により組成物は再び空気から酸素を吸収、電圧印加・解除により酸素を繰り返し発生できることを見い出した。

30 その後、酸素発生体の成分・組成と組成物の形態について鋭意検討した結果、特にコバルト(II)シップ塩基錯体またはメソテトラキス(α, α, α, α-ο-ビバルアミドフェニル)ポルフィリナトコバルト(II)イミダゾール錯体を55～85重量%の割合で含有する導電性カーボンとの混合組成物が上記目的に極めて優れた作用を有する、という実験結果を得た。

【0006】 この出願の発明は、このような知見を踏まえて完成されている。この出願の発明の原理的な要点は次のようにまとめられる。

40 (1) この発明の組成物を構成するコバルト錯体は、固相状態でも空気から酸素を選択的かつ可逆的に結合し吸収できる。

(2) 上記酸素結合反応は発熱反応である(反応にともなうエンタルピー変化はコバルト(II)シップ塩基錯体では約-30 kca l/mol)。コバルト(II)ポルフィリナトコバルト(II)イミダゾール錯体では約-15 kca l/mol)。すなわち酸素結合の平衡反応は低温で酸素吸収側、高温で酸素放出側にかたむく。

(3) 導電性カーボンとの特定組成の混合組成物は、適度な電気抵抗値をもち、極めて簡便な乾電池での電圧印

加で昇温して、それに応答して純酸素が発生する。

(4) コバルト錯体と導電性カーボンとの特定組成混合物を、ディスク状あるいはシート状に成形して両面より電圧印加すると、昇温すなわち酸素発生が速やかである。

(5) 電圧印加の解除により、組成物は降温、それに対応して空気から再び酸素を吸収する。すなわち酸素発生、吸収は電圧の印加・解除で繰り返し実施できる。

(6) 酸素吸収・発生は固相反応として生起するので、小型軽量・無溶媒の装置として構成できる。

【0007】

【発明の実施の形態】以上の特徴を有するこの出願の酸素吸収・発生体組成物の発明について、以下にその実施の形態を詳しく説明する。まず、この発明において用いられるコバルト錯体は、その代表例として2群あり、第1群はコバルト(II)シップ塩基錯体である。具体例を挙げると、N, N'-ビス(サリチリデン)エチレンジアミノコバルト(II)、N, N'-ビス(3-アルコキシサリチリデン)エチレンジアミノコバルト(II)、N, N'-ビス(サリチリデン)テトラメチルエチレンジアミノコバルト(II)、N, N'-ビス(サリチリデン)イミノジプロピルアミノコバルト(II)などがある。これらのコバルト(II)シップ塩基錯体は空気から酸素を選択的に結合し、Co/O₂ = 2/1の酸素付加体を可逆的に生成する。酸素結合(吸収)の速度は大きくはないが、シップ塩基錯体の合成は容易で、かつ酸素吸収・脱着の作動寿命は長い。

【0008】第2群はメソテトラキス(α, α, α, α-ο-ビバルアミドフェニル)ボルフィリナトコバルト(II)イミダゾール錯体である。このボルフィリナトコバルト(II)はCollmanらによって合成された化合物(文献としてJ.P.Collmanら、「J.Am.Chem.Soc.」97巻1427頁(1975))であり、適当なイミダゾール類と錯体を構成し、固相状態でも酸素結合能を発現する。イミダゾール類としてはN-メチルイミダゾール、N-ラウリルイミダゾール、N-ベンジルイミダゾール、N-トリチルイミダゾールなどが挙げられるが、昇温時の蒸散を防ぐため沸点が高く蒸気圧の低い誘導体で、かつ単位当たりの酸素吸収量の保持には分子量の小さい誘導体が望ましい。これらのボルフィリナトコバルト(II)イミダゾール錯体はCo/O₂ = 1/1の酸素付加体を生成し、酸素の脱着と再吸収は迅速である。

【0009】コバルト錯体と混合するカーボン粉末は、導電性であればいずれの製法によるものでもよい。必要に応じて石油エーテル類で洗浄し、乾燥した後、粉碎して用いる。カーボン粉末およびコバルト錯体の粒径は10~100μm程度が、両者の場合効率、電気抵抗、酸素ガスの透過性などの点から適当である。コバルト錯体は結晶であればこれを粉碎して上記粒径に整えて用いる。コバルト錯体とカーボン粉末の混合比は、コバルト

錯体の含量で5.5~8.5%が適当であるが、この範囲外を妨げるものではない。コバルト錯体含量とともに組成物当たりの酸素発生量は増加するが、電気抵抗値が大きく温度上昇が認められなくなる。例えば、N, N'-ビス(サリチリデン)エチレンジアミノコバルト(II)7.0%の組成物は、電気抵抗値3Ωで、6V印加により速やかに80°Cまで昇温し、酸素を発生する。メソテトラキス(α, α, α, α-ο-ビバルアミドフェニル)ボルフィリナトコバルト(II)ベンジルイミダゾール錯体6.0%の組成物は、抵抗値2Ωで、1.5V印加により直ちに85°Cまで昇温し酸素を発生する。

【0010】組成物はいずれの形状に成形してもよいが、メッシュ電極にはさんで通電し、短時間で組成物全体に昇温をもたらすには、ディスク状あるいはシート状が望ましい。例えば、組成物0.8gを銅メッシュにはさんで直徑2cmの円柱金型に充填し、3分間120kg/cm²で加圧すると、組成物のディスク(直徑2cm、厚さ2mm)が得られる。ディスク両面のメッシュ中央から導線を接続し、1.5乾電池(必要に応じて数個直列)で電圧印加すればよい。

【0011】なお、この発明による組成物は、単に酸素発生体としてのみならず、酸素吸収体など、広く空気からの酸素分離剤としての用途に供することができる。以下実施例を挙げて本発明をさらに具体的に説明する。

【0012】

【実施例】

実施例1

N, N'-ビス(サリチリデン)エチレンジアミノコバルト(II)(以下、Co(salen)と略記)は文献(M.Ca

lvinら「J.Am.Chem.Soc.」68巻2254頁(1946))に従い合成した。ビリジンから再結晶し、減圧下170°Cで1日加熱してビリジンを除去した。Co(salen)結晶を粉碎し、粒径を4.0~5.0μmに揃えた。導電性カーボン(藤倉化成カーボタイト、比重0.9~1.0)をヘキサン洗浄後、減圧下乾燥し、同じく粒径を4.0~5.0μmに揃えた。Co(salen)0.57gとカーボン0.23gを充分に混合し、白金メッシュにはさみ、3分間120kg/cm²加圧、Co(salen)カーボンのディスク(直徑2cm、厚さ2mm)とした。

X線マイクロ分析によるとコバルト元素の分布はディスク内で均一、またディスク破片のどの部分も均一に濃褐色に着色していたことから、Co(salen)とカーボンの良好な混和とCo(salen)の均一分散を確認した。Co(salen)ディスクの機械的強度は大きくはなかったが、後述の温度昇温(室温~80°C)および酸素ガスの吸収・放出実験での損傷は全くなかった。

【0013】ディスク両面の白金メッシュの中央から導線を接続し、ディスク状組成物の電気抵抗値を万能テスターで測定した。Co(salen)含量100、83、75、71、67%の組成物各々での抵抗値は無限大、2

000, 34, 3, 2Ωであった。電圧6V (1.5V乾電池4個直列) を印加し、ディスク内部の温度をサーミスタで測定した。1~2分後に一定温度に達し、Co(salen) 含量100, 83, 77, 71, 67%の組成物各々の内部温度は25(室温), 26, 55, 83, 50°Cであった。以上より、Co(salen) 含量80%以上の組成物ディスクは高抵抗で不適当、含量約70%のディスクは適度な導電性で、6V印加で速やかに80°Cまで昇温できた。

【0014】Co(salen) 含量71%組成物のディスクは室温大気下で22m1/g(ディスク)の酸素を吸収した。この吸収酸素量/Co(salen) モル比は0.49で、コバルトシップ塩基錯体への量論的な酸素結合反応による吸収である。この組成物ディスクの定常温度は印加電圧によって1~2分で上昇し、6V印加で80°Cに達した(3V, 4.5Vの印加では各々45°C, 60°C)。昇温に応答して、ディスク(Co(salen) 71%、直径2cm、厚さ2mm)から18m1の酸素ガスが発生した(同ディスクg当りでは22m1の酸素ガス)。

【0015】上記の酸素ガスの発生は1~2分で完了した。電圧印加の解除によりディスクはゆっくり降温し、空気から酸素を再び吸収した。この酸素再吸収には数時間を要した。6V印加による酸素ガスの発生と、電圧解除時の酸素再吸収は100回以上繰り返せた。また、酸素発生・吸収は、一酸化酸素、二酸化炭素、80%湿度によっても阻害されなかった。

実施例2

実施例1と同じく、Co(salen) 5.7gとカーボン2.3gを混合し、組成物を2×15cmの銅メッシュにはさみ、100kg/cm²加圧、シート状(2×15cm、厚み2mm)の成形体とした。シート両面の銅メッシュ片端から導線を引き出した後、シートをまるめ、2cm径2cm長のロールとした。導線を介して6V印加したところ、170m1の酸素ガスが約1分で発生した。

実施例3

N, N' - ビス(3-エトキシリチリデン)エチレン

ジアミノコバルト(II) (以下、Co(Esalen)と略記)を文献(実施例と同じCalvinらの文献)に従い合成した。実施例1と同じく再結晶、粉碎し、粒径を揃え、同じくカーボン粉末と混合、白金メッシュにはさみ直径2cm、厚さ2mmのディスクに成形した。

【0016】Co(Esalen)含量62%の組成物のディスクは、実施例1と同じく、6V電圧印加により約1分で80°Cまで昇温し、ディスクg当り18m1の酸素ガスを発生した。電圧印加の解除により、25分で同量18m1の酸素を空気から再吸収した。この酸素発生・吸収は100回以上繰り返せた。

実施例4

メソテトラキス(α, α, α, α-オーピバルアミドフェニル)ポルフィリナトコバルト(II) (以下、CoPと略記)を前記Collmanらの文献に従い合成した。無酸素下で、CoP0.31gとN-ベンジルイミダゾール0.25gのテトラヒドロフラン溶液30m1を調整、ヘキサン3m1を一時間おきに4回添加した後、静置した。CoPベンジルイミダゾール錯体(以下、CoP錯体と略記)の結晶が析出するので、ヘキサンで洗浄後、乾燥した。

【0017】実施例1と同じく、CoP錯体を約50μm粒径に揃え、同粒径カーボン粉末と混合した。銅メッシュにはさんで、120kg/cm²加圧によりディスク状に成形した。CoP錯体含量70, 65, 60%の各組成物ディスクの電気抵抗値は1.6, 1.5, 0.6Ωで、CoP錯体60%組成物は1.5Vの電圧印加で1分以内に88°Cまで昇温した。

【0018】CoP錯体60%組成物のディスクは、1.5V(乾電池1個)の電圧印加により、ディスクg当り6.5m1の酸素ガスを発生した。電圧解除により、約3分で同量6.5m1の酸素を空気から再吸収した。この酸素発生・再吸収は50回繰り返せた。

【0019】

【発明の効果】以上詳しく説明したとおり、この出願の発明によって、酸素ガスを電気信号により繰り返し発生することのできる小型軽量の無溶媒の成形体が提供される。